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## VII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.ON THE PRODUCTS OBTAINED BY THE ACTION OF  
NITRIC ACID UPON BROMTRINITROPHE-  
NYLMALONIC ESTER.

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Presented May 13, 1891.

OUR attention was first called to this subject by the appearance of a vivid red color, when common strong nitric acid was used to set free bromtrinitrophenylmalonic ester from its sodium salt, whereas no such color was observed if hydrochloric or sulphuric acid was used in place of nitric. Upon studying this action, we soon found that a new compound was formed, which could also be obtained from the free bromtrinitrophenylmalonic ester by treating it with hot nitric acid for a few minutes,\* or for some hours in the cold; the free ester therefore acts with nitric acid less readily than its salt, for with that the color appeared immediately. The further study of this compound (which was obtained in colorless prisms) proved that its formula was  $C_6HBr(NO_2)_3CNO_2(COOC_2H_5)_2$ ; that is, that it had been formed from the bromtrinitrophenylmalonic ester by replacing one of its atoms of hydrogen by the group  $NO_2$ . We have also obtained the following similar derivatives: from the bromdinitrophenylmalonic ester  $C_6H_2Br(NO_2)_2CNO_2(COOC_2H_5)_2$ , melting point  $111^\circ$ , and from the trinitrophenylenedimalonic ester  $C_6H(NO_2)_3CNO_2(COOC_2H_5)_2CH(COOC_2H_5)_2$ , also melting at  $111^\circ$ , so that the reaction seems to be a general one. The position of the group  $NO_2$  introduced by the action of nitric acid was determined by the study of the acidity of these compounds. In the bromtrinitrophenylmalonic ester  $C_6HBr(NO_2)_3CH(COOC_2H_5)_2$  there are only two atoms of hydrogen, one on the benzol ring, the other on the side-chain; if the first of these were replaced by  $NO_2$ , the effect, if any

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\* A preliminary account of this substance forms part of a paper by G. D. Moore, and one of us (these Proceedings, XXIV. 265). The statements made there are superseded by this paper.

would be to increase the acidity of the compound; whereas if the atom of hydrogen on the side-chain were replaced, the substance would cease to show acid properties, as the  $\text{NO}_2$  would have taken the place of the only atom of hydrogen which can be replaced by a metal. Upon studying the behavior of the new compound with alkaline reagents, we found that none of them affected it in aqueous solution, and that it was acted on only by sodic hydrate or ethylate in alcoholic solution, thus showing a marked contrast to the behavior of bromtrinitrophenylmalonic ester, which is acid enough to decompose sodic carbonate in aqueous solution. As just stated, sodic hydrate or ethylate does act upon our substance, but the red solution formed by the sodic ethylate was proved to contain sodic nitrite, and therefore the formation of the red salt was preceded by the removal of the group  $\text{NO}_2$ , which proves that this radical has replaced the hydrogen of the side-chain, as represented in the formula given above. This result was confirmed by the study of the compound  $\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)_2\text{CNO}_2(\text{COOC}_2\text{H}_5)_2$ , which proved even less susceptible to the action of alkalis than the corresponding trinitro compound. The replacement of the hydrogen in the malonic ester radical is not at all strange, since Franchimont and Klobbie\* have found that nitric acid converts malonic ester into nitromalonic ester.

To determine whether our substances were nitro compounds, that is, with the radical  $\text{NO}_2$  attached to the side-chain by its nitrogen, or nitrites, that is, with the radical attached by one of its atoms of oxygen, we considered in the first place the further action of nitric acid upon the compound  $\text{C}_6\text{HBr}(\text{NO}_2)_3\text{CNO}_2(\text{COOC}_2\text{H}_5)_2$ , which converted it after warming for three hours into  $\text{C}_6\text{HBr}(\text{NO}_2)_3\text{COH}(\text{COOC}_2\text{H}_5)_2$ , that is, the bromtrinitrotartronic ester; the reaction seemed to run smoothly, and the yield was 40 per cent of the theory. A similar change was produced by heat; when exposed to a temperature of  $124^\circ\text{--}126^\circ$ , the substance melted, turned blood-red, and gave off a great deal of gas, with a striking increase in volume at the same time.† A study of the gases showed that a part of the substance

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\* Ber. d. ch. G., XXIII., R. 62 from Rec. Trav. Chim., VIII. 283. For a discussion of the effect of different radicals upon the action of nitric acid on fat substances, see Franchimont, Ber. d. ch. G., XX., R. 689 from Rec. Trav. Chim., VI. 224, and Ber. d. ch. G., XXIII., R. 64 from Rec. Trav. Chim., VIII. 307.

† These phenomena shown by our substance in melting, as well as many of its other properties, are very similar to those observed by Gabriel in the cases of the benzylidenphthalidinitrite, Ber. d. ch. G., XVIII. 1255, and the ethinidiphthalidinitrite, Ber. d. ch. G., XIX. 837, which confirms the view that our substance is a nitrite.

had undergone complete decomposition, as they contained bromine; the residue, however, furnished a considerable amount of the substituted tartronic ester mentioned above. The action therefore has a certain resemblance to the conversion of the nitrate of tartaric acid into tartronic acid. These easy conversions of the compound containing the group  $\text{NO}_2$  into the corresponding tartronic ester can be best explained on the theory that this group is attached to the side-chain by oxygen, but cannot be considered as a strict proof of this point. Accordingly we have reduced with tin and hydrochloric acid the substance  $\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)_2\text{CNO}_2(\text{COOC}_2\text{H}_5)_2$  (selected because it can be obtained more easily than the trinitro compound), and have found that it yields ammoniac chloride and a substance having the formula  $\text{C}_6\text{H}_3\text{NH}_2(\text{CHOHCONH})\text{HCl}$ , that is, the chloride of amidoxindol; there can be no doubt, therefore, that the group  $\text{NO}_2$  is attached to the side-chain by one of its atoms of oxygen, and the substances are nitrites and not nitromalonic esters.

One of the most striking properties of the nitrite of bromtrinitrophenylmalonic ester is its slight stability. As has been already stated, it decomposes rapidly, with change of color and evolution of gas, at  $124^\circ$ – $126^\circ$ , but it is not necessary to heat to this temperature to bring about the decomposition, as it also takes place slowly at  $100^\circ$ , and partially even at  $70^\circ$ . Boiling with alcohol decomposes the substance completely, and boiling water produces a similar but less complete change. The nitrites of the corresponding dinitro compound and of the trinitrophenylenedimalonic ester are much more stable.

As has been stated above, the nitrite of bromtrinitrophenylmalonic ester, if warmed for three hours with strong nitric acid, or heated alone to its decomposition point, yields a product in which the radical of the nitrous acid has been replaced by hydroxyl, and which is therefore bromtrinitrophenyltartronic ester; this substance melts at  $156^\circ$ , and possesses marked acid properties. It is not necessary, however, to make it from the nitrite, as the bromtrinitrophenylmalonic ester is converted directly into it by warming for three hours with nitric acid. This therefore is a case of the direct oxidation of a tertiary hydrogen to hydroxyl,\* and, as we have succeeded in isolating the intermediate product, our work throws some light on the mechanism of the reaction, showing that it consists in the case of nitric acid of the formation of a nitrite, followed by its saponification to the hydroxyl compound.

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\* Richard Meyer, *Ann. Chem.*, CCXIX. 234, CCXX. 1; J. Bredt, *Ber. d. ch. G.*, XIV. 1780.

$\text{C}_6\text{H}(\text{C}_6\text{H}_5\text{NH})(\text{NO}_2)_3\text{CNO}_2(\text{COOC}_2\text{H}_5)_2$ , the nitrite of anilido-trinitrophenylmalonic ester, was obtained by the action of aniline on the corresponding bromine compound; it forms red rhombohedra, which melt at  $119^\circ$ , decomposing at one degree higher, and shows marked acid properties, which must be due to the effect of the three nitro groups upon the hydrogen attached to the nitrogen in the anilido group, since, as has been already stated, the corresponding bromine compound forms no salts. This conclusion was confirmed by the study of the anilidotrinitrotoluol, which contains no other hydrogen capable of being replaced by a basic radical, and yet formed the sodium salt  $\text{C}_6\text{CH}_3\text{H}(\text{C}_6\text{H}_5\text{NNa})(\text{NO}_2)_3$ . As was to be expected, however, this toluol compound was not so acid as the nitrite of anilidotrinitrophenylmalonic ester, which contains such a very negative radical in place of the methyl.

The anilidotrinitrotartronic ester was also made from the corresponding bromine compound, and was obtained in two modifications; one formed at higher temperatures appeared in orange-red prisms melting at  $143^\circ$ , the other in rounded masses of yellow needles melting at about  $122^\circ$ . Both show the same percentage composition on analysis, and one is easily converted into the other; the yellow into the red by allowing the alcoholic solution to crystallize at about  $60^\circ$ , by heating the solid a little below its melting point, or by boiling it with water; the red into the yellow by solution in glacial acetic acid and precipitation with water. Unfortunately we have not succeeded in determining the molecular weights of these substances, as we have not yet found a solvent that gives satisfactory results with Raoult's method. The work on these substances will be continued in this laboratory, especially with a view to determining whether the nitrogen is the cause of the isomerism (if they are not polymeres), but we may say now that this does not seem very probable to us on account of the striking resemblance in properties\* between our two substances and the two forms of benzilorthocarbonic acid described by Graebe.†

The anilidotrinitrophenyltartronic ester forms salts with one atom,  $\text{C}_6\text{H}(\text{C}_6\text{H}_5\text{NH})(\text{NO}_2)_3\text{COM}(\text{COOC}_2\text{H}_5)_2$ , or with two atoms of univalent basic radicals,  $\text{C}_6\text{H}(\text{C}_6\text{H}_5\text{NM})(\text{NO}_2)_3\text{COM}(\text{COOC}_2\text{H}_5)_2$ . To our great surprise, the disodic salt was formed even when the ester was present in large excess. This tartronic ester is much more strongly acid than the anilidotrinitrophenylmalonic ester (melting

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\* It is a curious fact that even the melting points are nearly the same.

† Ber. d. ch. G., XXIII. 1344.

point  $133^{\circ}$ ), a fact which confirms the formula assigned to it. We may add, that we have failed in all our attempts to convert anilido-trinitrophenylmalonic ester into its nitrite, or the corresponding tartronic ester, by the action of nitric acid.

We have also tried without success to convert the bromdinitrophenylmalonic ester into dinitrophenylenedimalonic ester by the further action of sodium malonic ester.

The remainder of the paper contains the experimental details of the work.

#### *Preparation of Tribromtrinitrobenzol.*

The experience gained in making tribromtrinitrobenzol for the work described in this paper has led us to introduce into the process given in previous papers \* from this Laboratory some improvements, which are described in this section.

To the preparation of tribromaniline we have nothing to add, but in the conversion of it into tribrombenzol we have found it best to proceed as follows:—50 gr. of dry tribromaniline were dissolved with the aid of heat in 300 c. c. of alcohol containing 75 c. c. of benzol to increase its solvent power, and 20 c. c. of common strong sulphuric acid added to the hot solution from a pipette. If this formed a precipitate, it was dissolved by longer heating, more of the solvents being added if necessary. 20 gr. of finely powdered sodic nitrite were then sifted into the hot liquid, as rapidly as the violence of the action would permit; after which the whole was heated until the effervescence had ceased, and, after standing over night, filtered, washed, and dried, when the product could be treated directly with nitric acid to make the tribromdinitrobenzol in the manner already described.† The yield of tribrombenzol was good, 42–44 gr. from the 50 gr. of tribromaniline. The filtrate and washings contained so little of the organic substance that it was not worth while to work them up.

In the conversion of this body into tribromtrinitrobenzol we have found the cause of the much larger yield obtained by Dr. Moore ‡ than by Dr. Wing.§ This does not depend so much on the larger proportion of fuming sulphuric acid used, as on the rapidity with which the boiling is carried on. To get the best yield we found it necessary to raise the mixture to the boiling point as quickly as possible, and to keep it boiling violently during the whole of the three hours. Under these conditions the yields varied from 8 to 10 gr. of tribromtrinitrobenzol from 20 gr.

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\* These Proceedings, XXIII. 139, XXIV. 258, 273.

† Ibid., XXIV. 274.

‡ Ibid., XXIV. 258.

§ Ibid., XXIII. 140.

of tribromdinitrobenzol, that is, 36 to 45 per cent of the theoretical, if both the nitric and fuming sulphuric acids were of the best quality. To prove that this violent boiling was the cause of the large yields, in one experiment the mixture was allowed to stand in the cold for a week, and then kept barely at the boiling point for seven hours, when it yielded only 18 per cent of the tribromtrinitrobenzol.

*The Nitrite of Bromtrinitrophenylmalonic Ester,*  
 $C_6HBr(NO_2)_3CNO_2(COOC_2H_5)_2$ .

This substance was prepared as follows:— 3 gr. of bromtrinitrophenylmalonic ester\* were mixed with about 10 gr. of nitric acid, specific gravity 1.38, and warmed in a dish for three minutes on the water bath, when both the undissolved organic substance and the acid became intense blood-red; the mixture was then allowed to cool, the acid liquid poured off, and the solid residue warmed once more for two minutes with about the same volume of fresh acid. After this, the acid was decanted off, and the solid crystalline product washed with water till free from nitric acid, which changed it from a deep blood-red to a pale reddish-white color. The purification of this substance gave us much trouble at first on account of its slight stability, since even the short warming necessary to dissolve it in alcohol was sufficient to decompose it partially, while longer heating with alcohol produced complete decomposition; but at last we obtained satisfactory results from the following method. The crude substance, after the thorough washing with water mentioned above, was dissolved in warm chloroform, in which it is freely soluble, but even with this solvent care must be taken to warm the mixture for as short a time as possible; it was advisable, therefore, to achieve the solution rather by the use of a larger quantity of chloroform than by using a smaller volume at a higher temperature. This chloroform solution was then diluted with about its own volume of common alcohol, when the substance gradually separated in well formed white prisms, and was obtained pure after two of these crystallizations. It must be dried *in vacuo*, as it decomposes on the water bath; in fact, even the temperature of a steam radiator (about 70°) was sufficient to bring about a partial decomposition.

A small additional amount of this substance could be obtained from the red nitric acid mother liquors formed in its preparation, either by adding water or by evaporating them to dryness; but this quantity is

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\* Melting at 104°. These Proceedings, XXIV. 258.

so small that it is not worth the amount of work necessary to free it from the red viscous impurity with which it is mixed, especially as the mother liquors can be used to more advantage for the preparation of the bromtrinitrophenyltartronic ester made by the longer action of hot nitric acid on bromtrinitrophenylmalonic ester.\*

The same substance was formed when the bromtrinitrophenylmalonic ester stood in the cold with nitric acid of specific gravity 1.38 for three days. At first there was no visible change, but after two hours the mixture began to show a red color, which increased in intensity to a deep blood-red. The product was purified in the way just described, but this method of making it is on the whole not so good as that at a temperature of 100°.

The ease with which the substance breaks up under the influence of heat rendered the combustion of it a matter of great difficulty, since we encountered at one time an almost explosive evolution of gas, and at another the formation of a partial vacuum in the tube. The latter we are inclined to ascribe to the sudden absorption by the plumbic chromate of the large quantity of bromine given off by the substance. We finally succeeded in getting good results by spreading out the weighed portion through the whole length of a long porcelain boat, and then applying the heat so gradually that a layer of not more than a few millimeters of it melted at any one time. Care was also taken that the temperature did not rise much above 115° until the whole of the substance had been melted, after which the combustion was finished in the usual way without trouble.

The analyses led to the following results:—

- I. 0.2157 gr. of the substance gave on combustion 0.2514 gr. of carbonic dioxide and 0.0496 gr. of water.
- II. 0.1978 gr. of the substance gave 0.2310 gr. of carbonic dioxide and 0.0428 gr. of water.
- III. 0.1978 gr. of the substance gave 0.2324 gr. of carbonic dioxide and 0.0430 gr. of water.
- IV. 0.2014 gr. of the substance gave 20.6 c. c. of nitrogen at a temperature of 24° and a pressure of 772.6 mm.
- V. 0.1890 gr. of the substance gave 18.6 c. c. of nitrogen at a temperature of 19° and a pressure of 752.8 mm.

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\* On one occasion the acid mother liquors yielded by spontaneous evaporation large white prisms, which melted in the crude state at about 99°, and were apparently somewhat soluble in water; but, although we have tried in many ways, we have not succeeded in obtaining this substance a second time.



VI. 0.2101 gr. of the substance gave by the method of Carius  
0.0813 gr. of argentic bromide.

VII. 0.2078 gr. of the substance gave 0.0792 gr. of argentic bromide.

VIII. 0.2054 gr. of the substance gave 0.0776 gr. of argentic bromide.

	Found.							
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Carbon	31.79	31.84	32.03					
Hydrogen	2.56	2.40	2.42					
Nitrogen				11.66	11.20			
Bromine						16.47	16.22	16.08

These analytical results agree best with the percentages required by a substance formed from the bromtrinitrophenylmalonic ester by replacing one of its atoms of hydrogen by the radical  $\text{NO}_2$ , as is seen from the following table.

	Calculated for $\text{C}_6\text{HBr}(\text{NO}_2)_3\text{CNO}_2(\text{CO}_2\text{C}_2\text{H}_5)_2$ .	Found. Mean.
Carbon	31.52	31.88
Hydrogen	2.22	2.46
Nitrogen	11.32	11.43
Bromine	16.16	16.26

Our reasons for the position assigned to the radical  $\text{NO}_2$  in this formula, and for supposing that it is not a nitro group ( $-\text{N} \equiv \text{O}_2$ ), but a nitrite ( $-\text{O} - \text{N} = \text{O}$ ), have been already stated in the introduction to this paper. The yield is satisfactory on the whole; 5 gr. of bromtrinitrophenylmalonic ester gave 3.26 gr. of the substance,\* instead of the 5.5 gr. required by the calculation, that is, 59 per cent of the theoretical yield.

*Properties of the Nitrite of Bromtrinitrophenylmalonic Ester.* — It occurs usually in short thick well developed glistening white prisms, with terminations consisting of two planes at both ends, which seem to indicate that the crystals belong to the monoclinic system. Less commonly the prisms are long and rather slender, with terminations similar to those of the shorter form. Its behavior when heated is very characteristic. If a tube containing some of it is dipped into an oil bath at  $124^\circ$ – $126^\circ$ , the substance turns red round the sides, then deeper, and the action gradually runs through the mass, until after a second or two the whole is melted forming a dark blood-red liquid, which occupies many times the volume of the original substance, and contains bubbles

\* In addition to this amount 0.7 gr. of bromtrinitrophenyltartronic ester was obtained from the mother liquors.

of gas. The action is evidently a decomposition, and can be produced at much lower temperatures, since if the tube containing the substance, instead of being dipped into the heated bath as described above, is gradually heated with the bath, the action takes place even below  $120^{\circ}$ . In fact, it can also be brought about by long-continued heating in the steam bath, or partially even at  $70^{\circ}$ . It is evident, therefore, that the compound has no definite melting or decomposition point, but yet the temperature given at first ( $124^{\circ}$ – $126^{\circ}$ ) can be used as such in purifying the substance, since it is essentially constant, if care is taken always to heat the samples examined in the same way.

This decomposition seemed so interesting that we examined it more carefully. For this purpose a considerable quantity of the nitrite of bromtrinitrophenylmalonic ester was heated in a test tube inserted in an air bath, and the gaseous products of the reaction drawn through a solution of baric hydrate. At  $103^{\circ}$ – $108^{\circ}$  there was a quantity of red vapor given off, and a precipitate of baric carbonate formed in the tubes containing the baric hydrate solution. The red vapor was recognized by the smell as bromine, and this was confirmed by the precipitation of argentic bromide when argentic nitrate was added to the acidified filtrate from the baric carbonate. On the other hand, we could not detect a trace of nitrate or nitrite with ferrous sulphate and sulphuric acid. After the substance had been heated to  $103^{\circ}$ – $108^{\circ}$  for three hours, the temperature was raised to  $125^{\circ}$  for two hours and a half, but the additional loss at this higher temperature was very small. We intended originally to determine quantitatively the amounts of the various products, but abandoned this idea when we found that the loss was not constant, three experiments giving 25 per cent, 30 per cent, and 21 per cent respectively. The appearance of the bromine, too, shows that there has been a complete decomposition of a part of the substance, and therefore the volatile products are of so little interest that we did not care to spend the time necessary for the identification of the others, which must have been formed in addition to the bromine and carbonic dioxide. On the other hand, we were much interested in the non-volatile product of the reaction left in the test tube as a fused rather viscous mass of a brownish red color, in which crystals were embedded. It was purified by washing several times with alcohol, which removed much of the viscous portion, then the residue was crystallized, first from dilute, and finally from common alcohol, and when pure showed the melting point  $156^{\circ}$  and the crystalline form of the bromtrinitrophenyltartronic ester described later in this paper. The action of heat on our nitrite, there-

fore, is similar to the well known conversion of the so-called nitrotar-taric acid into tartronic acid.

The nitrite of bromtrinitrophenylmalonic ester is almost insoluble in cold water, perhaps a little more soluble in boiling water; but if the substance was boiled for some time with water, the crystals were converted superficially into a dark red oily substance, and the water gave a slight test for bromine; this decomposition seemed to be due, however, only to the heat (see above), not to the presence of the water. It is slightly soluble in cold, more freely in hot ethyl alcohol, but this solution is easily decomposed by heat, since boiling for fifteen minutes converts the substance completely into a brownish red viscous product resembling half-dried varnish, from which nothing definite could be isolated, and even a very short heating with alcohol is sufficient to form some of this viscous body. Its solubility in methyl alcohol resembles that in ethyl alcohol; it is freely soluble in chloroform, or acetone; soluble in benzol, or glacial acetic acid; slightly soluble in carbonic disulphide; very slightly in ether, and essentially insoluble in ligroine. The best solvent for it is the mixture of chloroform and alcohol described above. Strong sulphuric acid seems to have no action on it in the cold, or if heated, until the substance decomposes, when it dissolves forming a reddish solution; strong hydrochloric acid has no action on it, either hot or cold, as long as the substance does not decompose; strong nitric acid has little or no action on it in the cold, even when allowed to stand with it for some weeks, when heated to  $100^{\circ}$  it converts it gradually into the bromtrinitrophenyltartronic ester, as is described in detail later in this paper under the preparation of that substance.

Ammonic hydrate acts on it little, if at all, even when the action is assisted by the addition of alcohol; sodic hydrate in aqueous solution has no action, but if alcohol is added the crystals begin to dissolve slowly, imparting a red color to the liquid but only a partial solution is effected in the cold. From this observation we inferred that no salt was formed until the nitrite was decomposed, and to test the accuracy of this inference we treated some of the nitrite with an alcoholic solution of sodic ethylate, which gave at once a dark blood-red coloration; but even here only a part, and that not the larger part, of the crystals of the nitrite was dissolved; the red solution poured off from the unaltered crystals gave a good test for a nitrite with starch paste, potassic iodide, and dilute sulphuric acid, with ferrous sulphate and sulphuric acid, and by Liebermann's reaction, so that there can be no doubt that sodic nitrite was formed in the experiment.

This proves the correctness of our inference that the substance melting at  $124^{\circ}$ – $126^{\circ}$  cannot form salts ; and the blood-red salt observed must have been derived from the decomposition product left after the removal of the group  $\text{NO}_2$  from our substance. It may be added, that acid or neutral sodic carbonate has no action on the nitrite in aqueous solution, and very little, if any, in presence of alcohol.

*Nitrite of Anilidotrinitrophenylmalonic Ester,*  
 $\text{C}_6\text{H}(\text{C}_6\text{H}_5\text{NH})(\text{NO}_2)_3\text{CNO}_2(\text{COOC}_2\text{H}_5)_2$ .

Aniline acts with great violence on the nitrite of bromtrinitrophenylmalonic ester. If the substances are mixed at ordinary temperatures, the action is almost explosive, a good part of the mixture is thrown out of the beaker, and the product seems to be principally carbon. If the mixture is kept cool by immersing the beaker in water, the action goes more mildly, but the product is still very black and impure. We therefore carried on the reaction in ethereal solution with the best results as follows :— 1 gr. of the nitrite of bromtrinitrophenylmalonic ester was mixed with a small quantity of ether, and, disregarding the fact that a portion of the crystals had not dissolved, a slight excess of aniline was added ; the ether at once turned red, and the undissolved crystals of the nitrite were taken up, while aniline bromide was deposited in their place. At the end of a few minutes the reaction was complete, and, after washing out the aniline and aniline bromide with water containing a little hydrochloric acid, the ether was allowed to evaporate, when it left a vivid red mass, which was purified by dissolving it in hot chloroform avoiding long heating, and then adding alcohol until the crystals began to separate, as it had been found that this substance, like the corresponding bromine compound, was decomposed by heating with alcohol. After the substance showed the constant melting point  $119^{\circ}$  it was dried *in vacuo* for analysis.

The combustion of this substance was even more difficult than that of the bromine compound, as it decomposed with almost explosive violence at a temperature a few degrees above its melting point, and did not begin to decompose at all at lower temperatures. We were unable therefore to burn it in an open tube, but at last got satisfactory results by using a closed tube, mixing it with a long layer of plumbic chromate and applying the heat very gradually. Its analyses led to the following results :—

- I. 0.1542 gr. of the substance gave on combustion 0.2538 gr. of carbonic dioxide and 0.0678 gr. of water.

II. 0.1494 gr. of the substance gave 18.9 c. c. of nitrogen at a temperature of 24°.3 and a pressure of 752.3 mm.

	Calculated for $C_6H(C_6H_5NH)(NO_2)_3CNO_2(CO_2C_2H_5)_2$	I.	Found. II.
Carbon	44.97	44.88	
Hydrogen	3.35	4.88	
Nitrogen	13.80		14.02

In spite of the unsatisfactory number for the hydrogen, these results prove that the substance has the formula which we have assigned to it. The yield was good, 0.9 gr. of the nitrite of the bromtrinitrophenylmalonic ester giving 0.7 gr. of the anilido compound, instead of the 0.92 gr. required by the theory, that is, 76 per cent.

*Properties.* — The nitrite of the anilidotrinitrophenylmalonic ester is a very beautiful substance, crystallizing in rhombohedra often two millimeters long and one millimeter thick, with a very acute angle, which is frequently, but not always, truncated by a basal plane. The color of the crystals by reflected light is a rich full red, somewhat darker than that of chromic anhydride, by transmitted light orange-red. It melts at 119°, turning black and giving off a few bubbles of gas, if the temperature has not risen above this point; but at 120° it decomposes with such violence that frequently a good part of the substance is thrown out of the capillary melting tube. It is essentially insoluble in cold water, and its solubility does not seem to be increased by heat; very slightly soluble in cold ethyl alcohol, more soluble in hot, but still not freely, the hot solution seems to undergo partial decomposition; more soluble in methyl alcohol, whether cold or hot, than in ethyl alcohol, but not freely even in this; very freely soluble in chloroform; freely in benzol, or acetone; soluble in glacial acetic acid; slightly in ether, or carbonic disulphide; insoluble in ligroine. The best solvent for it is a mixture of chloroform and alcohol. Strong sulphuric acid seems not to act on it in the cold, but when heated with it the substance decomposes, and then dissolves with a blackish color; strong nitric acid does not act on it in the cold, but when hot dissolves it with a yellow color; strong hydrochloric acid has no action on it, whether cold or hot.

The nitrite of anilidotrinitrophenylmalonic ester showed marked acid properties. Acid sodic carbonate in aqueous solution had no action with it, but, if assisted with alcohol, gave a red solution; potassic carbonate behaved in the same way; sodic hydrate turned the crystals black, forming at the same time a brownish solution, which on addition of alcohol became deeper and blackish red, turning in

time to blackish brown; ammoniac hydrate in aqueous solution gave a red color, but the action was not complete until alcohol was added, when a very dark red solution was formed. The nitrite of anilidotri-nitrophenylmalonic ester therefore shows much more acid properties than the corresponding bromine compound, which is indifferent to all these reagents except sodic hydrate in presence of alcohol, and this fact puzzled us at first, until we decided that the hydrogen attached to the nitrogen in the anilido radical ( $C_6H_5NH$ ) might be rendered acid by the presence of the three nitro groups. That this is the correct explanation of the phenomenon we have proved by preparing and analyzing the sodium salt of anilidotrininitrotoluol, which contains no atom of hydrogen that could be replaced by sodium except the one attached to the nitrogen of the aniline radical. The description of this work will be found in the following section.

An attempt to analyze the sodium salt of the nitrite of anilidotri-nitrophenylmalonic ester gave no satisfactory result, owing undoubtedly to the partial formation of sodic nitrite from the organic nitrite by the action of the sodic hydrate used in making the salt.

*Sodium Salt of Anilidotrininitrotoluol*,  $C_6H_3H(C_6H_5NNa)(NO_2)_3$ .

To prepare this salt, 1 gr. of anilidotrininitrotoluol\* (melting point  $151^\circ$ ) was dissolved in alcohol, and mixed with an alcoholic solution of 0.09 gr. of sodic hydrate, that is, over 0.03 gr. less than the amount required to convert the gram of substance into its salt; a little ether was then added, and the solution of the salt evaporated rapidly to dryness in a narrow beaker sunk throughout its whole length in the steam bath. During the evaporation there was an odor of phenylisocyanide. The dry mass was washed thoroughly with benzol to remove the excess of anilidotrininitrotoluol, the residue dried at  $100^\circ$ , and analyzed. As the salt explodes when heated with strong sulphuric acid, it should be dissolved in water, treated with dilute sulphuric acid, filtered, and the filtrate evaporated to dryness and converted into neutral sodic sulphate.

0.7876 gr. of the salt gave 0.1662 gr. of sodic sulphate.

	Calculated for $C_6H_3H(C_6H_5NNa)(NO_2)_3$ .	Found.
Sodium	6.76	6.84

The salt prepared as described above forms a maroon-black powder, which explodes gently when heated alone, or with strong sulphuric

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\* These Proceedings, XXIV. 255.

acid, forming in the latter case a very loose spongy blackish mass. It is soluble in alcohol with a yellowish brown color like that of ferric chloride; insoluble in ether, or benzol; water decomposes the salt almost completely, forming a yellow precipitate and a pale brown solution, which is strongly alkaline. The action of the anilidotrinitrotoluol with alkaline reagents was also studied, and, as was to be expected, no action was obtained with acid, or neutral carbonate of sodium, or ammoniac hydrate in aqueous solutions; but if the action was assisted by the presence of alcohol, each of these reagents gave a barely perceptible reddish coloration, so slight in the case of ammoniac hydrate that we were doubtful whether there had been any action; sodic hydrate in aqueous solution gave a slight yellow coloration, which, on the addition of alcohol, was at once converted into a very dark blood-red. The acid character of the anilidotrinitrotoluol therefore is much less marked than that of the nitrite of anilidotrinitrophenylmalonic ester, and as the position of the anilido group with regard to the nitro groups is the same in both compounds, we must ascribe this to the presence of the nitrite of the malonic ester radical  $\text{CNO}_2(\text{COOC}_2\text{H}_5)_2$ , with its large amount of oxygen in place of the indifferent methyl contained in the toluol.

*Bromtrinitrophenyltartronic Ester*,  $\text{C}_6\text{HBr}(\text{NO}_2)_3\text{COH}(\text{COOC}_2\text{H}_5)_2$ .

If the nitrite of bromtrinitrophenylmalonic ester, or the ester itself, was heated for some time with nitric acid, it was converted into the corresponding tartronic ester, which we found it convenient to prepare as follows:—1 gr. of bromtrinitrophenylmalonic ester was mixed with about 10 c. c. of nitric acid of specific gravity 1.38, and heated on the water bath for three hours in a dish covered with a watch-glass, fresh nitric acid being added when necessary to replace that lost by evaporation. At the end of this time the substance was found to be completely dissolved in the small quantity of hot nitric acid left, but upon cooling colorless crystals separated, which, after washing with water, were essentially the pure substance, one recrystallization from alcohol being all that was needed to make them melt at  $156^\circ$ , the constant melting point of this compound. If, as was usually the case, the bromtrinitrophenylmalonic ester was contaminated with acetylenetetracarboxylic ester, a yellowish oil was also formed, which however remained dissolved in the nitric acid mother liquor. The amount of the substituted tartronic ester in this mother liquor was so small that it did not pay for the working up.

The bromtrinitrophenyltartronic ester can also be made from the

nitrite of the corresponding malonic ester, but this method has no advantage over the preparation direct from the malonic ester described above, except in the case of the nitric acid mother liquors from making the nitrite, which yield on longer heating with nitric acid a small amount of the tartronic ester, and this is worth saving on account of the tedious and costly preparation of the mother substance.

The substance dried *in vacuo* was analyzed with the following results:—

- I. 0.1951 gr. of the substance gave on combustion 0.2380 gr. of carbonic dioxide and 0.0584 gr. of water.
- II. 0.2049 gr. of the substance gave 16.2 c. c. of nitrogen at a temperature of 17°.5 and a pressure of 763.7 mm.
- III. 0.2044 gr. of the substance gave according to the method of Carius 0.0836 gr. of argentic bromide.
- IV. 0.2272 gr. of the substance gave 0.0930 gr. of argentic bromide.

	Calculated for $C_6HBr(NO_2)_3COH(CO_2C_2H_5)_2$ .	I.	II.	Found. III.	IV.
Carbon	33.47	33.28			
Hydrogen	2.58	3.33			
Nitrogen	9.02		9.20		
Bromine	17.17			17.41	17.42

Our reasons for considering this a tartronic ester rather than a phenol have been given already in the introduction to this paper. The yield is satisfactory, considering the amount of loss to be expected from such a method of preparation; 1 gr. of bromtrinitrophenylmalonic ester gave 0.4 gr. of the substance, or about 40 per cent of the theoretical yield.

*Properties.* — The bromtrinitrophenyltartronic ester crystallizes from alcohol in long white prisms, terminated by planes at a very obtuse angle to each other, so that the ends look almost but not quite square. These crystals are often arranged in radiating groups, and in that case are generally much more slender than when occurring in isolated prisms. It is deposited from its solution in hot nitric acid in rather sharp slender needles. It melts at 156°, and is nearly but not quite insoluble in water, whether hot or cold; soluble in cold alcohol, freely in hot; rather more soluble in methyl than in ethyl alcohol; freely soluble in benzol, glacial acetic acid, or acetone; soluble in ether, and somewhat more so in chloroform; nearly insoluble in carbonic disulphide; insoluble in ligroine. The best solvent for it is hot alcohol. Strong sulphuric acid has no action upon it in the cold, but if hot, dissolves



it with difficulty with a reddish brown color; strong hydrochloric acid has no action on it hot or cold in open vessels, but decomposes it if the two substances are heated together in a sealed tube; nothing could be obtained from the products, however, except a mass like a dry varnish, which we did not succeed in bringing into a state fit for analysis. An exactly similar result was obtained in an attempt to saponify it with sulphuric acid of specific gravity 1.44. Strong nitric acid has no action on it at first, whether cold or hot, but if heated with it for some time seems to destroy it completely, and a similar result was obtained upon boiling it with bromine and water, as in both these cases we could not succeed in isolating any organic oxidation product.

Acid sodic carbonate in aqueous solution had no action on bromtrinitrophenyltartronic ester, but on the addition of alcohol a pale red color appeared, which became more marked on standing; potassic carbonate also did not affect it in aqueous solution, but gave a strong dark red solution on addition of alcohol; aqueous sodic hydrate turned the crystals brown, and dissolved some of them with a brownish color; on the addition of alcohol all the substance went into solution with a dark red color; ammoniac hydrate gave a red solution, but the action was not complete until alcohol was added, when the solution became very dark red. The bromtrinitrophenyltartronic ester therefore showed the strong acid character which we should expect, but no attempt was made to analyze its salts, as it was found that the bromine atom was removed by alkaline solutions with great ease, sodic bromide being formed, when it was treated with sodic ethylate even in the cold.

*Anilidotrinitrophenyltartronic Ester,*  
 $C_6H(C_6H_5NH)(NO_2)_3COH(COOC_2H_5)_2$ .

This substance was made by adding an excess of aniline to solid bromtrinitrophenyltartronic ester; the reaction ran smoothly with a slight evolution of heat, and was complete after the mixture had been allowed to stand for a few minutes, when the aniline bromide and excess of aniline were removed by washing with very dilute hydrochloric acid, and the bright yellow residue purified by crystallization from alcohol. At first rounded masses of radiating needles looking like little balls of fat of a bright yellow color were obtained, but as the crystallization continued, orange-red prisms began to appear, and increased in quantity until after several recrystallizations the greater part of the substance had been converted into this form. This behavior during

crystallization suggested to us that the substance probably occurred in two modifications, which was proved to be the case by the determination of the melting points of the two sorts of crystals, the yellow, after thorough purification, melting at about  $122^{\circ}$ , the red at  $143^{\circ}$ . As the substance passes from one form to the other with great ease, many experiments were necessary in order to find methods for obtaining each in a state of purity.

*Red Modification of Anilidotrinitrophenyltartronic Ester.*

To obtain this form from the crude product of the reaction it was crystallized several times from alcohol, until a mixture of the two forms rich in the red had been obtained, and then a strong alcoholic solution of the mixed crystals was allowed to evaporate slowly at temperatures from  $50^{\circ}$  to  $70^{\circ}$ . The product thus obtained, which showed no sign of the yellow form, was dried at  $100^{\circ}$ , and analyzed with the following results : —

- I. 0.1792 gr. of the substance gave on combustion 0.3114 gr. of carbonic dioxide and 0.0694 gr. of water.
- II. 0.2016 gr. of the substance gave on combustion 0.3534 gr. of carbonic dioxide and 0.0809 gr. of water.
- III. 0.1938 gr. of the substance gave 19.9 c. c. of nitrogen at a temperature of  $22^{\circ}$  and a pressure of 767.7 mm.

	Calculated for $C_6H(C_6H_5NH)(NO_2)_3COH(CO_2C_2H_5)_2$ .	I.	Found. II.	III.
Carbon	47.69	47.40	47.80	
Hydrogen	3.77	4.30	4.46	
Nitrogen	11.71			11.76

The air-dried red crystals lost only 0.19 per cent when dried at  $100^{\circ}$ , and therefore were free from water or alcohol of crystallization.

*Properties.* — The red form of anilidotrinitrophenyltartronic ester crystallizes in well formed prisms, often half a centimeter long, with at each end a pyramidal termination consisting of four planes. It has an orange-red color like that of potassic dichromate, and melts at  $143^{\circ}$ ; is essentially insoluble in cold water, very slightly soluble in boiling water, forming a pale yellowish solution; soluble in cold alcohol, rather freely in hot. This solution if allowed to evaporate at temperatures from  $50^{\circ}$  to  $70^{\circ}$  deposits crystals of the red modification, as has been already stated; but if allowed to evaporate at ordinary temperatures, a mixture of red and yellow crystals is usually obtained, although occasionally only red crystals are formed under these con-

ditions. The red modification is more soluble in methyl than ethyl alcohol; very freely in acetone. Both these solutions deposit some yellow crystals. Soluble in ether or chloroform; slightly soluble in cold benzol, freely in hot. The solution in benzol or chloroform deposits the substance in a viscous state. It is slightly soluble in cold glacial acetic acid, more soluble in hot; from this solution it is usually precipitated by the addition of water in the yellow form, although once or twice we thought we obtained the red modification; very slightly soluble in carbonic disulphide; insoluble in ligroine. Strong sulphuric acid when cold has no action on it, but dissolves it with a brownish yellow color when hot; strong nitric acid dissolves it partially when cold with a yellow color, and the action is increased by heating; cold hydrochloric acid has no action on it, but dissolves it very slightly when hot.

*Yellow Modification of Anilidotrinitrophenyltartronic Ester.*

This substance was most conveniently obtained from the mixture of the two forms, after it had been purified by several crystallizations from alcohol, by dissolving it in warm glacial acetic acid, and, after allowing the solution to stand for some hours, precipitating the solid matter by the addition of water. The yellow powder thus obtained was dried at ordinary temperatures over sulphuric acid, and analyzed with the following results:—

- I. 0.1879 gr. of the substance gave on combustion 0.3284 gr. of carbonic dioxide and 0.0726 gr. of water.
- II. 0.1924 gr. of the substance gave 20.5 c. c. of nitrogen at a temperature of 25° and a pressure of 769.7 mm.

	Calculated for $C_6H(C_6H_5NH)(NO_2)_3COH(CO_2C_2H_5)_2$	Found.	
		I	II.
Carbon	47.69	47.66	
Hydrogen	3.77	4.29	
Nitrogen	11.71		12.05

The substance dried over sulphuric acid lost no weight when heated to 100°, showing that it contains neither water nor alcohol of crystallization.

*Properties.*—The yellow form crystallizes in very fine needles united into spherical groups like those of wavellite, looking frequently like little balls of fat, and has a full yellow color like that of potassic chromate. It is hard to determine the melting point with accuracy, because this form is quickly changed into the red modification, at least

in part, when heated to a few degrees below that temperature; it is necessary therefore to heat the bath up to the melting point before immersing the capillary tube containing the substance; under these conditions it melts, and then changes to the red form, and solidifies again, after which it does not melt until about  $140^{\circ}$ . The melting point we ascribe to this substance is  $122^{\circ}$ , but we are not sure that this is accurate to one degree. This change from yellow to red can also be brought about slowly by heating at  $100^{\circ}$ , by boiling the yellow form with water for some time, or most conveniently by crystallization from alcohol at temperatures from  $50^{\circ}$  to  $70^{\circ}$ . In its solubility in the different solvents the yellow form does not differ much from the red, but seems in general to be more soluble.

We have made many attempts to determine the molecular weights of the two modifications by the method of Raoult, but have not as yet succeeded in finding any solvent which gives satisfactory results. Acetic acid, owing to its conversion of the red into the yellow form, could at best give results only for the latter, but a number of determinations showed us that it was of no use even for this purpose, as results were obtained varying from 295 to 345 (the theoretical molecular weight is 478), therefore showing that some reaction (probably the formation of an acetoxymalonic ester) had taken place between the acetic acid and the ester. An experiment with phenol gave an excellent result with the red form, 477 instead of 478; but with the yellow only 307 was obtained, indicating a chemical action similar to that observed with acetic acid, and we are not inclined to accept any result with phenol, however excellent it may appear, as with a substance which is so easily affected by solution as this there can be no certainty that it has remained in the same modification, unless it can be recovered directly from the solution used, and this we have found no means of doing in the case of phenol. Benzol gives such uncertain results with substances containing a hydroxyl group,\* that we did not think it worth while to try it. We have hopes that naphthaline† may give the desired result for the red form; this will be tried in this Laboratory, and a further attempt made to find a satisfactory solvent for the yellow modification; but as the departure of one of us from Cambridge makes it necessary to postpone further work in this direction until next year, we have thought it best to publish at once our present results, which have already reached a certain completeness.

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\* Ber. d. ch. G., XXI. 707.

† Ber. d. ch. G., XXII. R. 128.

*Salts of Anilidotrinitrotartronic Ester.*

The anilidotrinitrotartronic ester has well marked acid properties. An aqueous solution of acid sodic carbonate has essentially no action on it, but if alcohol is added there is a slight but distinct action indicated by the change of color; potassic carbonate gives in aqueous solution a slight red color, which becomes a strong red if alcohol is added; sodic hydrate in aqueous solution gives a very dark red, apparently converting the substance completely into its salt; ammoniac hydrate also gives a strong red color, which is intensified on the addition of alcohol. Some of the alkaline salts were studied more carefully with the following results.

*Monopotassium Salt,  $C_6H(C_6H_5NH)(NO_2)_3COK(COOC_2H_5)_2$ .*

This salt was made by adding 20 c. c. of absolute alcohol to 0.5 gr. of the ester, and then a large excess of pure potassic carbonate; carbonic dioxide was given off, the solution became very dark red, and after digesting the substances for eight to ten minutes with the occasional aid of a little heat, the dark brown solution was filtered from the excess of potassic carbonate, evaporated to dryness in a beaker sunk throughout its whole length in the steam bath, and analyzed with the following results:—

- I. 0.3458 gr. of the salt heated with strong sulphuric acid gave 0.0548 gr. of potassic sulphate.  
 II. 0.3748 gr. of the salt gave 0.0696 gr. of potassic sulphate.

	Calculated for	Found.	
	$C_6H(C_6H_5NH)(NO_2)_3COK(CO_2C_2H_5)_2$ .	I.	II.
Potassium	7.58	7.11	8.34

The absolute alcohol used in the second analysis had not been freshly prepared, and the slight excess of potassium can be accounted for by the assumption that it had absorbed a little water.

*Properties.* — The acid potassic anilidotrinitrophenyltartronic ester, when prepared by the method described above, forms a brownish black amorphous solid, freely soluble in water or alcohol, slightly soluble in ether, and insoluble in benzol. The solutions have a dark brown color.

*Disodium Salt,  $C_6H(C_6H_5NNa)(NO_2)_3CONa(COOC_2H_5)_2$ .*

This salt seemed to be formed, to our great surprise, by the action of an alcoholic solution of sodic hydrate on an excess of the anilidotrinitrophenyltartronic ester. To prepare it, about 0.7 gr. of the ester

were mixed with a little alcohol, and somewhat less than the amount of sodic hydrate (also in alcoholic solution) necessary to form a mono sodium salt; a little ether was then added to the dark red solution, which was evaporated rapidly to dryness, the small beaker containing it being sunk throughout its length in the steam bath. After this the excess of unaltered ester was extracted with benzol, and the salt dried at  $100^{\circ}$ , and analyzed with the following results: —

- I. 0.2596 gr. of the salt gave after evaporation and ignition with sulphuric acid 0.0672 gr. of sodic sulphate.  
 II. 0.2848 gr. of the salt gave 0.0698 gr. of sodic sulphate.

	Calculated for $\text{C}_6\text{H}(\text{C}_6\text{H}_5\text{NNa})(\text{NO}_2)_3\text{CONa}(\text{CO}_2\text{C}_2\text{H}_5)_2$ .	Found.	
		I.	II.
Sodium	8.81	8.39	7.94

These results agree with the percentage corresponding to the formula as nearly as can be expected, when it is remembered that the salt was not crystallized, or purified in any other way; but still we cannot feel that they do more than make it highly probable that this is the composition of the salt, as it is certainly strange that a neutral salt should have been formed when such an excess of the acid substance was present, and we had no means of proving that the substance analyzed was a pure salt rather than a mixture; in fact, we observed a slight smell of phenylisocyanide during its preparation, indicating a deep decomposition of part of it, — only a very small part, however, if we may judge from the smell.

*Properties.* — The salt prepared as described above formed a dark reddish brown to black amorphous mass, soluble in water or alcohol; slightly soluble in ether; insoluble in benzol. Its solutions have a brownish red color.

The behavior of a solution of the ammonium salt of anilidotrinitrophenyltartronic ester, made by adding ammoniac hydrate to an excess of the ester, although it smelt strongly of ammonia, was tested with various reagents and gave the following characteristic precipitates: —

With a *zinc salt*, orange-brown.

With a *manganese salt*, brown.

With a *cadmium salt*, reddish brown.

With a *copper salt*, yellowish brown.

With a *lead*, *mercuric*, or *silver salt*, reddish brown.

The fact that the ammonium salt gives no precipitate with salts of magnesium, calcium, strontium, or barium, is also highly characteristic.

Although, as has been already stated, no definite results were ob-

tained from our attempts to oxidize or saponify the bromtrinitrophenyltartronic ester, we thought that perhaps the anilido compound might behave better, and accordingly the following experiments were made, in the hope (unfortunately not realized) of decomposing the anilidotrinitrophenyltartronic ester into substances which would confirm our inferences in regard to its nature. The substance was allowed to stand in the cold with an aqueous solution of potassic permanganate, but, although a considerable part of it disappeared, no organic oxidation product could be detected. In the hope of saponifying the ester, we added to it an excess of sodic hydrate dissolved in water, and allowed the reddish brown solution thus formed to stand in a corked flask at ordinary temperatures for some weeks. During this standing a strong odor of phenylisocyanide was developed, and, if the amount of ester was small, the color changed to yellow; if, on the other hand, the quantity was large, it retained its dark brown color; at the end of the experiment, nothing was obtained except a brown precipitate of most unpromising appearance, formed by adding an acid to the solution, and the phenylisocyanide already mentioned as recognized by its smell. As the formation of this substance would necessitate a complete destruction of the benzol ring which carried the nitro groups and malonic ester radical, we did not think it worth while to repeat the experiment.

This formation of an isocyanide from the destruction of a benzol ring containing nitro groups by means of an aqueous solution of sodic hydrate recalls the work of Post and Hübner,\* who found that ordinary dinitrobenzol when boiled with a solution of sodic or potassic hydrate was decomposed with formation of a cyanide quickly if the solution was strong, slowly if it was dilute. They also found that picric acid behaved in the same way, thus confirming the earlier observation of Wöhler.†

*Anilidotrinitrophenylmalonic Ester,*  
 $\text{C}_6\text{H}(\text{C}_6\text{H}_5\text{NH})(\text{NO}_2)_3\text{CH}(\text{COOC}_2\text{H}_5)_2.$

This substance was made to see whether it would be possible by treatment with nitric acid to convert it directly into either its nitrite or the anilidotartronic ester described above. It was found, however, that standing for several days at ordinary temperatures with strong nitric acid produced complete decomposition of part of the substance, the only product insoluble in the acid being unaltered anilidotrinitro-

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\* Ber. d. ch. G., V. 408 (1872).

† Pogg. Ann., XIII. 488 (1828).

phenylmalonic ester; and that upon heating it on the steam bath with nitric acid for three hours in the hope of making the anilidotrinitrophenyltartronic ester, the substance was destroyed completely, oxalic acid being the only product which we could find. It seems therefore that the less acid anilido compound cannot be converted into the nitrite or tartronic ester. But although these attempts to oxidize the substance have failed, we add the description of the anilidotrinitrophenylmalonic ester, which has not been prepared heretofore.

It is easily made by adding an excess of aniline to solid bromtrinitrophenylmalonic ester. The reaction ran smoothly in the cold with slight evolution of heat, and the product was purified by washing with very dilute hydrochloric acid to remove the excess of aniline and the aniline bromide, and crystallization from alcohol until it showed the constant melting point  $133^{\circ}$ , when after drying at  $100^{\circ}$  it was analyzed with the following result:—

0.1866 gr. of the substance gave 20.2 c. c. of nitrogen at a temperature of  $25^{\circ}.5$  and a pressure of 764.3 mm.

		Calculated for	
		$C_6H(C_6H_5NH)(NO_2)_3CH(CO_2C_2H_5)_2$	Found.
Nitrogen		12.13	12.12

*Properties.*—The anilidotrinitrophenylmalonic ester crystallizes in long slender sharp needles arranged in radiating bunches. It has a full yellow color, and melts at  $133^{\circ}$ . It is very slightly, if at all, soluble in cold water, more soluble in hot, as shown by the faint yellow color of the solution; freely soluble in hot alcohol, less so in cold; somewhat more soluble in methyl than in ethyl alcohol; very freely soluble in chloroform; freely in benzol or acetone; soluble in ether, or glacial acetic acid; slightly in carbonic disulphide; insoluble in ligroïne. Boiling alcohol is the best solvent for it. Strong sulphuric acid or nitric acid dissolves it slightly in the cold with a yellow color; the solubility is somewhat increased by heating; strong hydrochloric acid acts on it only very slightly, cold or hot. An aqueous solution of acid sodic carbonate has no action upon it, but there is a barely perceptible change of color if alcohol is added; aqueous potassic carbonate gives little if any action, but on the addition of alcohol a brown solution is formed, the action however seems to be incomplete; aqueous sodic hydrate turns the crystals dark and brown, the solution becoming yellow, the addition of alcohol seems to convert the substance completely into the sodium salt; aqueous ammoniac hydrate gives a barely perceptible yellow color, which is not increased by the addition of a little alcohol, but a large amount gives a dark brown solution.



A solution of the sodium salt of anilidotrinitrophenylmalonic ester made by adding a drop of sodic hydrate to an excess of the ester moistened with alcohol, and then diluting largely with water, gave characteristic precipitates with the following reagents:—

With a *calcium salt*, a heavy reddish brown precipitate.

With a *strontium salt*, a slighter precipitate.

With a *barium salt*, a very faint precipitate.

A *magnesium salt* gives a reddish brown precipitate, as heavy as that obtained with the calcium salt.

With a *manganese salt*, reddish brown flocks.

With a *zinc salt*, yellowish brown.

With a *cadmium salt*, orange-yellow.

With a *copper salt*, yellowish brown.

With a *lead salt*, reddish brown.

With a *silver salt*, dark reddish brown.

Its most striking property is that the barium salt is the most, the calcium salt the least, soluble of its salts with metals of the second group, and in this respect it resembles its mother substance, the bromtrinitrophenylmalonic ester,\* the corresponding acetacetic ester,† and the orthonitrobenzoylmalonic ester of Bischoff.‡

*Nitrite of Trinitrophenylenedimalonic Ester,*  
 $\text{C}_6\text{H}(\text{NO}_2)_3\text{CH}(\text{COOC}_2\text{H}_5)_2\text{CNO}_2(\text{COOC}_2\text{H}_5)_2.$

After we had studied the action of nitric acid on the bromtrinitrophenylmalonic ester, it seemed of interest to determine whether the dimalonic compound acted in the same way, and accordingly we proceeded as follows. A small quantity of the trinitrophenylenedimalonic ester § (melting-point  $123^\circ$ ) was covered with nitric acid of specific gravity 1.38, and warmed in a dish on the steam bath for two minutes; the solid turned dark yellow, and melted to a drop of oil. The acid was then allowed to cool, poured off, and replaced by the same quantity of fresh acid, when it was warmed as before for three minutes, making five in all. Upon standing, the oily product solidified to a mass of crystals, which were washed thoroughly with water, and at first recrystallized from alcohol; but as in each crystallization a small quantity of yellow oil was formed, we feared a partial decomposition, and resorted to the method which had given excellent results in the purification of the nitrite of bromtrinitrophenylmalonic ester, that is,

\* These Proceedings, XXIV. 261.

‡ Ann. Chem., CCLI. 362.

† Ibid., 278.

§ These Proceedings, XXIV. 268.

dissolving the substance with very little heat in chloroform, and then adding enough alcohol to start the separation of crystals; in this way a pure substance melting at  $111^{\circ}$  was obtained without difficulty, which was dried at about  $70^{\circ}$  and analyzed with the following results:—

- I. 0.1960 gr. of the substance gave on combustion 0.3012 gr. of carbonic dioxide and 0.0714 gr. of water.  
 II. 0.1926 gr. of the substance gave 16.7 c. c. of nitrogen at a temperature of  $23^{\circ}$  and a pressure of 771 mm.

	Calculated for $\text{C}_6\text{H}(\text{NO}_2)_3\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{CNO}_2(\text{CO}_2\text{C}_2\text{H}_5)_2$ .	Found	
		I.	II.
Carbon	41.81	41.91	
Hydrogen	3.83	4.05	
Nitrogen	9.76		9.93

The substance is therefore the mononitrite of trinitrophenylenedimalonic ester.

*Properties.*—The substance crystallizes in rather thick plates with parallel sides terminated at each end by two planes at an acute angle to each other, these acute angles being usually, but not always, truncated by planes at right angles to the parallel sides. The crystals are often much twinned and grouped into very irregular forms. It has a lemon-yellow color, and melts without decomposition at  $111^{\circ}$ . It is very slightly soluble in boiling water, giving a pale yellow solution, essentially insoluble in cold; slightly soluble in cold alcohol, freely in hot; more soluble in methyl than in ethyl alcohol, whether cold or hot; both these solvents seem to produce a slight decomposition of the substance when heated with it; very freely soluble in chloroform; freely soluble in benzol, or acetone; soluble in ether, or glacial acetic acid; slightly soluble in carbonic disulphide; insoluble in ligroine. The best solvent for it is the mixture of chloroform and alcohol used as described above. Strong sulphuric acid has no action on it in the cold, but, when heated with it, dissolves some of it with a pale yellow color after it melts; strong hydrochloric acid has no apparent action on it either hot or cold; strong nitric acid has no action on it in the cold, but dissolves it slightly when hot, and if heated with it for two hours and a half destroys it completely, the only product which we isolated being oxalic acid; on one occasion, however, another product melting near  $140^{\circ}$  was obtained in small quantity, but we did not feel sufficiently interested in this part of the subject to prepare enough of it to determine whether it was the dinitrite or a tartronic ester. One thing, however, these experiments have established, namely, that the

dimalonic compound is less stable toward nitric acid than the brom-malonic compound, since the latter, after three hours' boiling with the acid, had not gone further than the tartronic ester, while the former usually underwent a total decomposition. On the other hand, the nitrite of the dimalonic compound is not decomposed by melting, and only slightly by heating with alcohol, and therefore in these two respects is more stable than the nitrite of bromtrinitrophenylmalonic ester.

The nitrite of trinitrophenylenedimalonic ester shows acid properties. With an aqueous solution of acid sodic carbonate it gives no action, and very little when alcohol is added, unless in very large quantity, when a yellowish solution is formed; with potassic carbonate in aqueous solution there is no action, but on the addition of alcohol a very strong yellowish brown color; aqueous sodic hydrate gives a reddish solution, on the addition of alcohol an orange flame-colored solution, entirely different in color from that given with the potassic carbonate; ammoniac hydrate imparts a strong yellow coloration to the solution, intensified on the addition of alcohol. Upon comparing the acidity of this substance with that of the trinitrophenylenedimalonic ester, it seems as if this latter substance were somewhat more acid than the nitrite, since it gives a slight coloration with aqueous potassic carbonate, and seems to act more easily with acid sodic carbonate and alcohol, but the difference between the two in this respect is certainly very slight, which we should not have expected, as it seemed probable that the introduction of the nitrous acid radical (ONO) would have increased the ease with which the hydrogen in the other malonic ester radical was removed.

A solution of the sodium salt of the nitrite of trinitrophenylenedimalonic ester was made by adding one drop of sodic hydrate solution to a large excess of the ester moistened with alcohol, and, after the action had taken place, diluting with much water. The solution thus obtained was of the color of a solution of potassic dichromate, but much less strongly colored than the solutions of the salts of any of the related substances. Its action with the various reagents was tried, and the following characteristic precipitates observed:—

With *barium salt*, rather heavy yellow flocks.

With *mercurous* or *lead salts*, heavy yellow flocks.

With *silver* or *copper salts*, yellow flocks.

Salts of *calcium*, *strontium*, or *magnesium* gave only faint yellow precipitates, decidedly different from the heavy one produced by baric chloride.

*Nitrite of Bromdinitrophenylmalonic Ester,*

Although bromdinitrophenylmalonic ester does not change in color when heated with nitric acid, as has been stated more than once in previous papers\* from this Laboratory, it really is affected in the same way as the corresponding trinitro compound, being converted into its nitrite, but without the formation of the red secondary product which made the reaction so striking in that case. The substance was prepared as follows. A small quantity of the bromdinitrophenylmalonic ester (melting point  $75^\circ$ – $76^\circ$ ) was heated on the steam bath with nitric acid of specific gravity 1.38 for five minutes, or longer (as the same compound was obtained if the heating was continued three hours); there was at first no sign of a reaction except a slight evolution of nitrous fumes; but, as the heating continued, the undissolved solid melted, forming an oil drop, which after cooling solidified to a mass of crystals, while at the same time the acid liquid deposited crystals looking very much like those of the bromtrinitrophenyltartronic ester. All of these crystals were purified by recrystallization from boiling alcohol, until they showed the constant melting point  $111^\circ$ , when they were dried at about  $70^\circ$ , and analyzed with the following results:—

- I. 0.1973 gr. of the substance gave on combustion 0.2492 gr. of carbonic dioxide and 0.0510 gr. of water.  
 II. 0.2084 gr. of the substance gave 17.4 c.c. of nitrogen at a temperature of  $22^\circ$  and a pressure of 755.6 mm.

	Calculated for $\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)_2\text{CNO}_2(\text{CO}_2\text{C}_2\text{H}_5)_2.$	Found	
		I.	II.
Carbon	34.66	34.44	
Hydrogen	2.67	2.87	
Nitrogen	9.33		9.41

The substance therefore is the nitrite of the bromdinitrophenylmalonic ester, and not the corresponding tartronic ester, as we had expected from the long heating used in one of the methods of preparation, and from the fact that no difficulty was encountered in making the combustion of it.

*Properties.*—The nitrite of bromdinitrophenylmalonic ester crystallizes usually in thick rhombic crystal often one millimeter in each direction, which look somewhat like rhombohedra with a sharp acute angle, but are seen to be twins by the lines of twinning and stria-

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\* These Proceedings, XXIV. 6, 257.

tions; the obtuse angles on these crystals are often truncated. Less commonly with the characteristic forms just described, long flattened prisms occur, which are terminated by a single plane at a sharp acute angle, rarely by two. It is easy to see that the rhombic crystals could be formed by the twinning of these prisms. The crystals are very lustrous, of a white color, with a slight greenish cast, and melt at  $111^{\circ}$  without decomposition. The substance is essentially insoluble in cold water, very slightly soluble in hot; soluble in cold alcohol, more so, but still far from freely, in hot. It shows no signs of decomposition when boiled with alcohol. It is more soluble in methyl than in ethyl alcohol, cold or hot; very freely soluble in benzol, chloroform, or acetone; freely soluble in glacial acetic acid; soluble in ether or carbonic disulphide; nearly, if not quite, insoluble in ligroine. Hot alcohol is the best solvent for it. Strong sulphuric acid has no action on it in the cold, but when hot dissolves a little of the substance after it has melted; strong hydrochloric acid has no action, hot or cold; strong nitric acid has no action on it in the cold, but when hot dissolves a little of it, which is deposited on cooling. Neither acid sodic carbonate nor neutral potassic carbonate had any action with it, even in presence of alcohol; sodic hydrate in aqueous solution was without action; if alcohol was added, a portion of the substance dissolved slowly with a yellow color, but most of the white crystals were left unattacked; ammoniac hydrate in aqueous solution had no action, with alcohol little or none. The substance behaves, therefore, as we should expect, a salt being formed only by a reagent like sodic hydrate strong enough to remove the  $\text{NO}_2$  group attached to the side-chain.

The nitrite of bromdinitrophenylmalonic ester is much more stable than the corresponding trinitro compound, since it is not decomposed by boiling with alcohol, or at its melting point, or by boiling with nitric acid; for, as has been already stated, it could be made by boiling for three hours with nitric acid, whereas under these conditions the trinitro compound was converted into the tartronic ester. Nor did longer boiling of the dinitro compound with nitric acid produce the tartronic ester, as even after seven hours it showed the melting point of the unaltered substance  $111^{\circ}$ . As the trinitro tartronic ester had been obtained also by heating the corresponding nitrite, we tried the same experiment with the dinitro nitrite, and found that, when heated a few degrees above its melting point, it turned rather dark colored, and gave off bubbles of gas, in which bromine was recognized by the smell. The residue was oily, but after solution in

alcohol crystals were obtained which showed the characteristic rhombic form of the nitrite of bromdinitrophenylmalonic ester. This experiment therefore seemed to show that the action of heat consisted only in the complete decomposition of a portion of the nitrite of bromdinitrophenylmalonic ester, and, as it did not promise to give the desired tartronic ester, further work in this direction was abandoned.

*Reduction of the Nitrite of Bromdinitrophenylmalonic Ester.*

The conversion of the nitrite of bromtrinitrophenylmalonic ester into the corresponding tartronic ester by nitric acid, or by the action of heat, indicates that the group  $\text{NO}_2$  in the side-chain is attached to the molecule by oxygen instead of nitrogen, or, in other words, that the substance is a nitrite, and not a nitro compound; but, as we could not consider this a conclusive proof of the oxygen attachment, we have studied the reduction of a body of this class, selecting for this purpose the dinitro compound, because it is more easily prepared than the corresponding substance containing three nitro groups, and also because the product obtained from it by reduction would probably be more stable than one containing one more amido group.

Six grams of the nitrite of bromdinitrophenylmalonic ester divided into three lots of two grams each were mixed with granulated tin, strong hydrochloric acid, and a few drops of alcohol, and after adding a piece of platinum to accelerate the reaction, were allowed to stand on a steam radiator ( $50^\circ$ – $70^\circ$ ) until all the organic matter had dissolved, and no further action was observed, which happened usually in about an hour and a half. If quantities larger than two grams were used a very dark colored solution was obtained. The solution poured off from the excess of tin was freed from stannous and stannic chlorides by means of sulphuretted hydrogen, when a residue was obtained by evaporation of the filtrate, which gave off ammonia gas when treated with an alkaline hydrate, and formed a precipitate of ammoniac chloroplatinate with chlorplatinic acid; it evidently therefore contained ammoniac chloride in addition to the chloride of the organic base. The washings of the sulphide of tin, which were worked up separately from the filtrate, on the other hand, yielded crystals which showed only a very slight amount of ammoniac chloride by the same tests, and accordingly these crystals were dried at  $100^\circ$ , and analyzed with the following results:—

- I. 0.1980 gr. of the substance gave 25.25 c. c. of nitrogen at a temperature of  $23^\circ$  and a pressure of 764.8 mm.

II. 0.1954 gr. of the substance gave by the method of Carius 0.1480 gr. of argentic chloride.

	Calculated for $C_6H_3NH_3Cl(CHOHCONH)$ .	Found.	
		I.	II.
Nitrogen	13.96	14.47	
Chlorine	17.70		18.73

These results are not all that we could wish; but although they show the presence of the small amount of ammoniac chloride, which we had detected by the qualitative tests, they leave no doubt in regard to the composition of the organic substance, and therefore we have not thought it worth while to spend the great amount of time which would have been necessary to prepare a sample entirely free from ammoniac chloride; especially as these analyses prove that the group  $NO_2$  is attached to the side-chain by oxygen, since we obtained, by the reduction of the nitrite of bromdinitrophenylmalonic ester, ammoniac chloride and the chloride of amidoxindol instead of the chloride of diamidoxindol, which would have been formed if the group  $NO_2$  had been attached to the molecule by the nitrogen.

*Properties of the Chloride of the Amidoxindol,*  
 $C_6H_3NH_3Cl(CHOHCONH)$ .

This substance was obtained crystallized in rather large plates, usually in forms like a closed fan terminated by an obtuse angle, and set in rows one over the other with the obtuse angles parallel, or arranged in branching arborescent forms like coral; sometimes in thicker sharp prisms. It had a dark yellow color as we observed it; was soluble in cold water, more so in hot; slightly soluble in cold or hot alcohol, and insoluble, or nearly so, in most of the other solvents. The strong acids gave no striking reactions with it, except strong nitric acid, which turned it orange-red; but this seemed to be due to some nitrous acid in the nitric, as on the addition of sodic nitrite the color was much intensified. Sodic hydrate added to the aqueous solution gave a few brown flocks, evidently from decomposition of a part of the base; ammoniac hydrate gave a tolerably heavy flocculent precipitate, at first whitish, but turning brown on exposure to the air, but it showed no signs of crystallization, and with the small amount of substance at our disposal we have been unable to obtain the free base in any definite form. The chloride mixed with alcohol and some strong hydrochloric acid imparted after some time a dark red color to a piece of pine wood.

*Attempt to make Dinitrophenylenedimalonic Ester.*

The results just described having shown that the behavior of bromdinitrophenylmalonic ester toward nitric acid was not so different from that of the trinitro compound as we had at first supposed, it became of interest to determine whether other apparent differences between these two bodies were no better marked, and accordingly we tried to make the dinitrophenylenedimalonic ester by the method which had given good results with the trinitro compound as follows:— 3 gr. of bromdinitrophenylmalonic ester were dissolved in ether, and, after the addition of 1.5 gr. of malonic ester previously treated with 0.15 gr. of sodium in a large quantity of alcohol, the mixture was boiled under a return-condenser for three hours; at the end of this time the solution had turned deep red, and a little solid had separated. The product was treated with water and dilute sulphuric acid, the ether separated, and the aqueous liquid tested for sodic bromide, which it was found to contain in small quantity, but the crystals deposited by the ether melted after one crystallization at  $75^{\circ}$ – $76^{\circ}$ , the melting point of bromdinitrophenylmalonic ester. We infer from this experiment, therefore, that, although a little dinitrophenylenedimalonic ester may have been formed, its quantity was exceedingly small, and that the reaction, if it goes on at all, certainly takes place with much more difficulty in the case of the dinitro than in that of the trinitro compound.